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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Method of manufacturing Artificial Fibres

I, **OLE-BENDT RASMUSSEN**, of 18, Masnedogade, Copenhagen, Denmark, Danish subject, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved method of forming fine fibres from films or filaments which are relatively thick.

Methods have been known for a number of years, for forming fibres from films or thicker filaments of normally crystalline high polymers.

For example in British Patent No. 479,202, the method described is to first orient the material by stretching it in a longitudinal direction, and then split it by mechanical means such as twisting, brushing or rubbing.

In my earlier British Patent No. 810,001 an improved method of forming fibres in this way is described. In this method the oriented film or filaments are mechanically treated whilst in the swollen condition. Smoother filaments are obtained by this method. Acoustic waves may be used for the mechanical treatment.

In all these methods an external mechanical force is used to fibrillate the filament or film. However, it is not possible to form fibres from thick foils in this way without damaging the material. It has also been impossible to produce from thin foils fibres which are thinner than the thickness of the foil, except when orientation has been made in the viscous fluid state and the fibrillation performed by acoustic waves. This method is however, very slow. It is also impractical to use ultra-thin films.

I have now discovered a new method for the production of fibres from films and thicker filaments of normally crystalline high polymers and which can be used to produce fibres of diameter less than the thickness of the film.

According to the invention a method for the production of fine fibres from a relatively thick filament or film of a high molecular weight normally crystalline organic polymeric substance comprises treating a relatively thick, oriented filament or film of the material containing a uniformly distributed, foreign substance so that the foreign substance changes physically and/or chemically to produce an internal mechanical stress in the filament or film which at least weakens and preferably forms fissures in the filament or film, parallel with the direction of orientation, and thereafter if the filament or film is not already completely transformed into fibres, mechanically working the filament or film to cause it to split up into separate fine fibres.

The foreign substance which is caused to change in the process of the invention may be incorporated in the filament or film by mixing it with the polymer from which the filament or film is formed or by absorbing it into the filament or film after the latter has been made. The first method is of course particularly suitable when solids are used as the foreign substance and the second when gases or liquids are used.

As will be described more fully later there are a variety of ways of producing the physical and/or chemical change in the substance. For example the foreign substance may be solid which takes part in a chemical reaction in which as gas is liberated or the foreign substance may be treated to cause a change of state of it resulting in expansion. Another method is by expanding a gas which has been absorbed by the filament or film and a still further method is by dissolving or swelling a solid substance in a liquid which can penetrate the filament or film so that an osmotic pressure acts upon the filament or film.

The initial shape of the high polymer body is not of any significance except that it should be in a form capable of being stretched. Thus the term film and filament is intended to

[Price 3s. 6d.]

Price 4s 6d

include bands of the high polymer as well as hollow tubes of the material. Any normally crystalline high polymer can be used in the process of the invention. Examples of these are polyamides, regenerated cellulose, polyvinyl alcohol, other vinyl high polymers, polyesters and cellulose esters.

In many embodiments of the method of the invention a finely divided substance is distributed in the film or filament before the fibrillation takes place. In these embodiments the substance should be dispersed as uniformly as possible and should also be homogeneous in size. It is desirable that after orientation the cross sectional area of each particle should not exceed 10 times the cross sectional area of the desired fibres; the mutual distance of the particles should be at least five times the thickness of the fibres and not less than five microns. If larger particles are used the tensile strength of the fibres produced is lowered and if they are closer together the abrasion resistance is lowered. The cross-sectional area of each fissure produced should be at least one tenth of the cross sectional area of the fibre desired. The finely divided substances are preferably incorporated in the high polymer whilst it is molten, the film or filament then being formed by extrusion from the melt. The substances can however be added to a solution of the polymer but there is a risk of sedimentation resulting in an uneven distribution.

The film or filament is then oriented by conventional methods. It is possible to chemically convert the high polymer to a different material between orientation and fibrillation. For example oriented cellulose acetate may be saponified by known methods into cellulose without spoiling the orientation. A conversion of this sort may also take place during or after the fibrillation process. In some cases the oriented material may shrink during the fibrillation process and it may then be necessary to re-orient the material. It may also be an advantage to give the film or filament a stronger orientation than the fibres should have and afterwards decrease the orientation by swelling or heat treatment. Conversely it is also possible to give the material a weak orientation then to split it and finally to give it a strong orientation.

Although it is preferred that the internal mechanical stress generated by the treatment of the filament or film substance is high enough to create a fissure in the material this is not essential as it has been found that very little mechanical processing is necessary if the internal stress is only 25% of that necessary for the creation of a fissure. However, it is preferred that the internal mechanical stress is sufficiently high to commence the fibrillation without any external mechanical processing. External mechanical treatment will be required in most cases to complete the fibrillation pro-

cess but the best results are obtained if the disintegration by internal mechanical stress is carried as far as possible.

As stated above in one of the methods of the invention a finely divided solid substance takes part in a chemical reaction in which a gas is liberated. The finely divided substance can act in a variety of ways. Thus it can react with a liquid or a component thereof which can penetrate the film or filament, to liberate a gas or it can act as a catalyst for the decomposition of a substance or for the reaction of substances contained in a liquid which can penetrate the filament or film. In this case it is preferred to have the catalyst supported on a porous carrier which facilitates the release of the gas in the oriented material. Another method is by incorporating an easily reacting substance and decomposing it to form a gas by heating or irradiating the filament or film. It is preferred when using this method to selectively heat the finely divided substance to reaction temperature by passing the filament or film quickly through a zone in which it is subjected to an intensive beam of irradiation such as radio or supersonic waves, the particles and the treatment being of such nature that the energy is absorbed mainly by the finely divided substance or by the finely divided substance and its immediately surrounding portions of the filament or film. This method is of advantage when the finely divided substance decomposes at a temperature above the melting point of the high polymer. Explosive material can be used in this way.

The fibrillation may also be carried out by causing a change of state resulting in expansion of a substance dispersed in the filament or film. In this embodiment of the invention the incorporated substance is volatile and is relatively insoluble in the high polymer. The evaporation of the volatile substance is facilitated by the incorporation of porous particles. The evaporation preferably takes place quickly and may be carried out by heating the filament or film or by suddenly decreasing the pressure of the atmosphere surrounding the film or filament.

Expansion of a gas to create the internal stress necessary for fibrillation may be effected in several different ways. A finely divided porous carrier having a gas absorbed or adsorbed therein may be uniformly distributed through the filament or film and it is then expanded by heating the filament or film or reducing the pressure of the atmosphere surrounding it. The gas may be absorbed by the finely divided porous carrier immediately before the expansion by forcing the gas under elevated and preferably constant pressure into the interior of the film or filament. In this case the finely divided porous carrier initially may contain a liquid in which the gas is soluble. This method is particularly applic-

able to polyamides, regenerated cellulose or a stabilised polyvinyl alcohol. Carbon dioxide can be used with all three materials and ammonia can be used with stabilised polyvinyl alcohol and regenerated cellulose. After the gas has been absorbed the filament or film is preferably immediately passed into a zone of lower preferably constant pressure.

Osmotic pressure can also be used to disrupt the material. In this case a finely divided substance is incorporated in the filament or film which is then treated with a liquid which will dissolve or swell the substance. Salts can be used in this method. The liquid formed should not be capable of dissolving the high polymer. This method is particularly useful when used in conjunction with the method just described as it is possible to initiate fibre formation by osmosis and then complete the process by treatment with a gas under pressure followed by expansion of the gas.

In any of the methods which require alteration of the pressure of the atmosphere surrounding the filament or film, irradiation by acoustic or supersonic waves in a bath through which the filament or film is passed may be used to do this. The final frequency of the waves is preferably between 5 and 20 kilocycles but is initially higher.

Several of the methods described above involve treatment of the filament or film with a liquid. In these methods the film is usually swollen by this treatment. For example in the osmotic method described above the liquid used to dissolve the finely divided substance also swells the filament or film. The internal mechanical stress however is generated by the solution formed of the finely divided substance. The liquid alone will not cause the formation of the fissures.

In some cases it may be advantageous to treat the film or filament or film containing the uniformly distributed foreign substance to generate the internal mechanical stress when the film or filament is in a swollen condition. For example when a gas is absorbed into the filament or film under pressure better results are obtained if the filament or film is in a swollen condition before the treatment with the gas, as the gas more readily penetrates the film.

The invention will now be described in detail with reference to the following examples:—

EXAMPLE No. 1.

A tubular polycaprolactam foil of circumference 10 cm and 0.03 mm thickness is made by extrusion from a granulate with which had been mixed 0.5% dehydrated strontiumchloride or sodium sulphate in the form of a powder with a very homogenous size of granules, on an average respectively 3 and 5 microns. Microscopy shows that the granules are evenly distributed in the material. The foil is cold-

drawn and is kept heated to 180 degrees for a few minutes in order to increase the crystallinity, to make the boundary between crystalline and amorphous domains sharper so that the splitting-up capacity is increased. It is treated for several hours with about 3 n aqueous hydrochloric acid solution which dissolves the salt. The solution exerts an osmotic pressure on the material and also causes it to swell. The concentration of the hydrochloric acid has been determined exactly, by experiments aiming at determining the degree of swelling at which the oriented high polymer used has its highest cleaveableness. The foil is again microscopied, and it now turns out to be furrowed by relatively long and ductlike but closed pores parallel with the direction of orientation. Comparative tests show that the pores increase the splitting-up capacity considerably both when dry and swelled. Part of the oriented foil is cut into narrow bands which whilst still swollen are passed through an apparatus or device in which it is rubbed between two skin-surfaces. This treatment splits into a coherent network or fibres. Many of the fibres have smaller cross-sectional dimensions than the thickness of the oriented foil (which is about 0.05 mm). Comparative tests show that the pores have had a large influence on the fineness of the fibres.

EXAMPLE No. 2.

A narrow 0.03 mm thick band of polyvinylalcohol softened with glycerol and with the same excipients as mentioned in Example No. 1 is made by extrusion. The band is oriented at an increased temperature and treated with formaldehyde to improve the water resistance. It is treated with a weak hydrochloric acid solution, examined as in Example No. 1, and split-up by rolling and rubbing between skin-surfaces. The result of the examinations and the splitting-up are the same as in Example No. 1.

EXAMPLE No. 3

A narrow oriented band of polyvinylalcohol is made as in Example No. 2, but, containing 0.1% activated carbon instead of the easily soluble salts. Cupric sulphate had been precipitated beforehand in the carbon, which is of homogenous granule size, on average 3 microns. The oriented band is then treated with an aqueous solution of hydrochloric acid containing hydrogen peroxide and afterwards contains large fissures which cannot be explained simply as a result of the osmosis caused by the copper sulphate. They are due to the gas released in the catalytic decomposition of the hydrogen peroxide by the copper sulphate in the carbon.

EXAMPLE No. 4.

A narrow band 0.2 mm thick is made by extrusion of polyvinylchloride to which

1% salicylic acid had been added in the form of granules of homogeneous size, on average 2 microns. The temperature of the polyvinylchloride must be kept under the melting point of the salicylic acid. The band is strongly oriented at an increased temperature, and part of it is treated for 48 hours by a mixture of ethyl alcohol and acetone. This treatment produces an osmotic pressure around the salicylic acid granules. At the end of the treatment the band is filled with pores, and after drying it is split up into fine fibres by being rubbed and rolled between two rubber surfaces. The untreated part of the oriented band cannot be split-up into fibres by this mechanical treatment.

EXAMPLE NO. 5.

A band consisting of super-polymerized polycaprolactam without any additive (k-value 95) is manufactured by extrusion. Immediately afterwards while it is still melted or semimelted, it is oriented by means of a pair of rollers rotating in opposite directions pressed against each other. Both are heated to a point near the melting point of the superpolymerisate, preferably a little below that point, but then the process must be carried out so quickly that no crystallisation occurs until the band is oriented. The band is extruded on to one of the two rollers, which it follows until it has passed between them. Then it is transferred to the second roller which rotates with a faster peripheral speed than the first so that the band is oriented. Then the band, now c. 0.01 mm thick and c 10 cm wide, is led through a cooling set of rollers rotating at the same peripheral speed as the preceding one. The oriented band is annealed for crystallisation in 2 minutes by blowing nitrogen, at a temperature of 180° C., on it and is immersed for a minute in a swelling aqueous hydrochloric acid solution (cf. Example No. 1). The band is suspended slackly whilst still swollen in a closed container where it is exposed for a short time to carbon dioxide at a pressure of 50 ats. The pressure is abruptly released and the band is ruptured into fine fibres.

EXAMPLE NO. 6.

Part of the cold-drawn foil prepared in Example No. 1, and which has been subjected to the osmotic process but not mechanically processed, is cut into narrow bands and fibrillated as in Example No. 5.

EXAMPLE NO. 7.

A narrow, oriented band of polycaprolactam containing 0.5% silica gel is made as described in Example No. 5. The granule size of the silica gel is homogeneous, on average 1 micron. The gel has previously been made water-repellent by known methods. The material is led under slight tension through

a swelling aqueous solution of hydrochloric acid free of gases in which it is irradiated by supersonic waves of frequency 60 kcps. This treatment produces fissures in the band. The fibrillation is completed in another bath which additionally contains 2% dispersed talc and which is irradiated by sound waves of frequency 10 kHz. The band is carried through this bath in a slack condition. Exceedingly fine fibres are produced. A comparative test will show that the porous granules of silica gel have increased the effect of the acoustic treatment considerably.

The intensity of the waves in both baths is near the maximum value obtainable by atmospheric pressure in a bath of the indicated composition.

EXAMPLE NO. 8.

A 0.1 mm thick oriented filament of polycaprolactam containing 1% of the same strontiumchloride preparation as was used in Example No. 1, is made in a similar way as the band in Example No. 5. It is subjected to an osmotic process similar to that described in Example No. 1. Then it is leached in water, vacuum dried at 100°—to introduce air into the pores—and acoustically split into fibres as in Example No. 7.

EXAMPLE NO. 9.

A 0.05 mm thick foil of polyvinylalcohol containing 5% of Ag_2C_2 (silver acetylide) is cast from aqueous solution. The grains of Ag_2C_2 are all about 0.05 mm. The foil is cut to strips of 5 mm width which are oriented at an elevated temperature and dried quickly.

Finally each band is passed through a high intensity light beam, produced by focussing the light from a series of arc-lamps, 20 Kw in all. The beam is delimited by a variable shutter, the lenses are water-cooled, and cold air is blown on the strip. The temperature of the transparent plastic is only slightly elevated whereas the dark explosive grains of Ag_2C_2 are brought to detonation, and the material splits into fibres.

EXAMPLE NO. 10.

A narrow band 0.03 mm thick is made by extrusion from cellulose acetate containing 0.03% of the carbon powder which also was used in Example No. 3. It is strongly oriented by being stretched in hot steam, after which the band is saponified into cellulose, and is acoustically split into fibres as in Example No. 7. However the baths contain a swelling aqueous ammoniacal solution of CuSO_4 .

EXAMPLE NO. 11.

Part of an oriented cellulose band produced as in Example No. 10 is immersed in a solution of CuSO_4 and fibrillated as in Example

No. 5. However, ammonia at 15 ats. and 50° C. is used instead of carbon dioxide.

WHAT WE CLAIM IS:—

1. A method for the production of fine
5 fibres of a high molecular weight, normally crystalline organic polymeric material, which comprises treating a relatively thick, oriented filament or film of the material containing a uniformly distributed foreign substance so
10 that the foreign substance changes physically and/or chemically to produce an internal mechanical stress in the filament or film which at least weakens and preferably forms fissures in the filament or film, parallel with
15 the direction of orientation, and thereafter if the filament or film is not already completely transformed into fibres, mechanically working the filament or film to cause it to split up into separate fine fibres.
2. A method as claimed in Claim 1, in
20 which the foreign substance is a finely divided solid substance which was uniformly dispersed in the polymeric substance from which the filament or film was formed and said substance takes part in a chemical reaction in
25 which a gas is liberated.
3. A method as claimed in Claim 2, in which the finely divided solid substance is reacted with a liquid or a component thereof
30 which can penetrate the film or filament to release a gas.
4. A method as claimed in Claim 2, in which the finely divided solid substance acts as a catalyst for the decomposition of a sub-
35 stance or the reaction of substances contained in a liquid which can penetrate the filament or film, to produce the gas.
5. A method as claimed in Claim 4, in which the finely divided substance is a catalyst
40 for the decomposition of hydrogen peroxide, and the filament or film is treated with an aqueous solution of hydrogen peroxide.
6. A method as claimed in Claim 2, in which the finely divided substance is decom-
45 posed to produce a gas by heating or irradiation of a filament or film.
7. A method as claimed in Claim 6, in which the finely divided substance is heated
50 to reaction temperature selectively by passing the filament or film quickly through a zone in which it is subjected to an intensive beam of irradiation (such as radio or supersonic waves) the particles and the treatment being
55 of such nature that the energy is absorbed mainly by the finely divided substance or by the finely divided substance and its immediately surrounding portions of the filament or film.
8. A method as claimed in Claim 1, in
60 which the treatment of the foreign substance uniformly distributed in the filament or film causes a change of state resulting in expansion of said foreign substance.
9. A method as claimed in Claim 8, in
65 which the substance previously incorporated is

a volatile substance which is vaporised and expelled from the filament or film by rapidly heating the filament or film, or reducing the pressure of the atmosphere surrounding the filament or film.

10. A method as claimed in Claim 9, in which a finely divided solid porous substance added to the polymeric substance from which the filament or film was made is present to facilitate and localise the release of the volatile substance.

11. A method as claimed in Claim 1, in which the foreign substance uniformly distributed in the filament or film is a gas which has been absorbed by the filament or film and which is caused to expand by heating the filament or film or by reducing the pressure of the atmosphere surrounding the filament or film.

12. A method as claimed in Claim 11, in which a finely divided solid porous carrier is present in the filament or film to increase the quantity of gas absorbed by the filament or film.

13. A method as claimed in Claim 12, in which the finely divided porous carrier contains a liquid in which the gas is soluble.

14. A method as claimed in any of Claims 11 to 13, in which elevated and preferably constant pressure is used to cause the absorption of the gas by the filament or film.

15. A method as claimed in any of Claims 11 to 14, in which when the filament or film is a polyamide the gas is carbon dioxide or when it is a regenerated cellulose or a stabilised polyvinyl alcohol, the gas is carbon dioxide or ammonia.

16. A method as claimed in Claim 14 or 15, in which the film or filament containing the absorbed gas is immediately passed into a zone of lower and preferably constant pressure.

17. A method as claimed in Claim 1, in which the foreign substance uniformly distributed in the filament or film is a finely divided solid which is dissolved or swollen by a liquid which can penetrate the filament or film so that an osmotic pressure acts upon the filament or film.

18. A method as claimed in Claim 17, in which the finely divided substance is a salt.

19. A method as claimed in Claim 17 or 18, in which the filament or film is dried after treatment, and then further treated by introducing a gas into the filament or film at elevated pressure and then expanding the gas by reducing the pressure of the atmosphere surrounding the filament or film.

20. A method as claimed in any of Claims 9 to 16 or 19, in which the alteration of the pressure of the atmosphere surrounding the filament or film is effected by the action of acoustic or supersonic waves in a bath through which the filament or film is passed.

21. A method as claimed in Claim 20, in

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which the final frequency of the waves is between 5 and 20 kilocycles but is initially higher.

- 5 22. A method of forming fibres from a film or filament of a high molecular weight normally crystalline organic polymeric substance, substantially as described herein with reference to any examples.

23. Fibres whenever produced by a process as claimed in any preceding claim.

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